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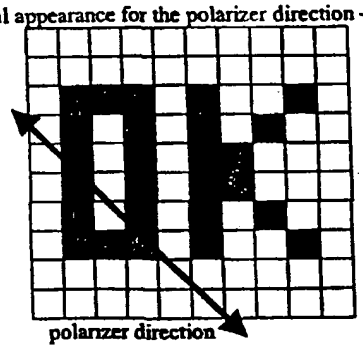
Combination of the Leuco dye (white base) and Cholesteric LPP/LCP device enables the recognition resp. the verification of the correct information of the cholesteric LPP/LCP security device (here the letters OK are shown): optical appearance for the polarizer direction –45°: positive image



(57) Abstract

Erasable and re–writable panel comprising an additional optical device which contains normally hidden images. These images can be made visible by specific techniques without changing the information of that panel. Furthermore, the panel containing the permanent visible information can be erased and re–written without alteration of the said additional optical device.

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Item Carrying Rewritable Visible Information

This invention relates to an item carrying rewritable visible information. Such an item can be, or can be an element incorporated into, an object such as a high-security ticket, pass, label or pre-paid debit card, which can thereby be (repeatedly) personalised, or whose use can increase security in authenticating branded goods, or which can be used in innovative decorative packaging.

Existing erasable and re-writable cards can in many cases be easily copied leading consequently to a severe restriction in their possible fields of application, although they have the advantages of cheapness and thinness.

According to the present invention, there is provided an item carrying rewritable visible information, characterised by a normally hidden image which can be revealed by means which do not tend to rewrite the visible information.

The means for revealing the normally hidden image may, for example, be to view it (with light) through a polariser. This would not carry any risk of degrading the visible information. On the other hand it is possible to change the normally visible information of the panel without alteration of the normally hidden image.

The normally hidden image may be carried in at least one optically anisotropic layer having regions with different preferred directions, e.g. in a liquid crystalline medium. Preferably, the optically anisotropic layer is formed with cross-linked liquid crystalline monomers or pre-polymers.

The item according to the invention may comprise an orientation layer for liquid crystal molecules, which may be formed of a linearly photopolymerised polymer network.

The rewritable visible information is preferably carried in a thermosensitive recording material, and may accordingly comprise a leuco dye and developer.

The visible information may co-operate with the normally hidden image to reveal other information

The techniques of linear photopolymerisation (LPP) - synonymous with photooriented polymer network (PPN) in other literature - and liquid crystal polymers

(LCP) (together LPP/LCP technology) allow the manufacturing of novel type of visual items containing normally hidden images which can be made visible by specific techniques. Backgrounds and manufacturing of such items are disclosed in, for example, US-A-5389698, EP-B-525473, EP-B-611981, EP-A-689084, EP-A-689065 and WO-A-98/52077.

Additionally to LPP/LCP optical devices disclosed in above mentioned patents many other types are imaginable which can be also included in the "item" described in this patent.

A particular use of these items is to protect against forgery and copying and for simple yet unambiguous document authentication. Further such items can be utilised also in the field of decorative packaging.

For example in the field of plastic cards (smart cards, telephone cards, credit cards, tickets, ...) an erasable and re-writable display incorporated in these said cards will significantly benefit the user (e.g. it is possible to know the purpose of such a card or ticket; e.g. its validity for a specific mentioned connection, or the amount of credit remaining on it, by simply reading the card). One possibility to manufacture such kind of cards which combine erasable and re-writable displays and magnetic stripes is disclosed e.g. in following patents:

- USA 5,686,382 (Appl. No. 556,021): Filed 1995/11/13, Issued 1997/11/11
  Thermal Recording structure and method of thermal recording;
  Assignees: Ricoh Company Ltd., Tokyo, Japan.
- USA 5,278,128 (Appl. No. 029,043); Filed 1993/03/10; Issued 1994/01/11;
  Reversible thermosensitive recording material
  Assignees: Ricoh Company Ltd., Tokyo, Japan.
- USA 5,158,924 (Appl. No. 760,007); Filed 1991/09/13; Issued 1992/10/27;
  Reversible thermosensitive recording material and image display method of using them
  Assignees: Ricoh Company Ltd., Tokyo, Japan.

This invention will now be described by way of example with reference to the accompanying drawings in which:

Fig 1 is a schematic view of an erasable and rewritable panel with permanent visible information,

Fig 2 is a schematic illustration showing the configuration of an optical component according to the invention, including a normally hidden image and an erasable and rewritable panel with permanent visible information.

Figs 3 and 4 show alternative forms of an item according to the invention with a hidden optical device,

Fig 5 shows an example of a set-up of the combination of a leuco dye type erasable and rewritable film and structured cholesteric LPP/LCP security device,

and Fig 6 illustrates the optical performance of the combination of a leuco dye type erasable and rewritable film and structured cholesteric LPP/LCP security device, according to the invention, with Figs 6A, 6B and 6C of Figure 6 showing the device in different states.

A re-writable thermosensitive recording material is composed of a support and a reversible thermosensitive recording layer formed thereon, which is capable of recording and erasing images repeatedly by utilising its property that the transparency can be changed reversibly from a transparent state to an opaque state, and vice versa, depending upon the temperature thereof (e.g. below 100°C the film becomes opaque, above 125°C the film becomes transparent). The reversible thermosensitive recording layer is composed of a reversible thermosensitive layer and a protective layer formed thereon. Images are reversibly formed and erased on this reversible thermosensitive recording material.

A commercial available magnetic reader with thermal printer/eraser head from Panasonic (Model KU-R12001A) was used to erase and rewrite information onto the card which include such a thermochromic layer and magnetic stripes. Such cards (thermochromic film FB 651-M) can be purchased from Ricoh Company Ltd., Tokyo, Japan. The film has an erasable and re-writable thermosensitive layer with metallic contrasting background on one side and a magnetic layer on the other, shown schematically in Figure 1, and consists of the following layers:-

from the base upwards: protective layer – magnetic layer – PET (polyethylene terephthalate) substrate – Al evaporated layer – thermochromic layer – protective layer.

The item according to the invention can be made up from the simultaneous utilisation of the two above described optical tools.

Onto an erasable and re-writable panel such as described above, an optical LPP/LCP device was added by the techniques described in the first list above of patents and further explained here:

1. Spin-coating (also other coating techniques can be applied) of suitable orientable linearly photopolymerisable (LPP) layer such as cinnamic acid derivatives or ferulic acid derivatives illustrated in patent publications EP-A-611786, WO 96/10049 and EP-A-763552 onto the protective layer of above described erasable and re-writable panel. For description in more detail, see below.
2. This LPP layer with a thickness of about 50nm is exposed through a photo mask to polarised light of different directions, namely 0° and 45° (0° means parallel to one edge of the substrate; other angles are also possible): this enable the storing of images and/or other information into the LPP layer.
3. Thereafter, this LPP layer is coated with a cross-linkable liquid crystal monomer or pre-polymer mixture (LCP) which shows birefringence, such as LCP mixture M_{LCP} described in more detail later. M_{LCP} has an optical anisotropy Δn of 0.13 leading to a film thickness of 1 μm for $\lambda/4$ retarder plates. The LCP material adopts the alignment (if any) of the immediately underlaying region of the LPP layer. The whole is then exposed to unpolarised (isotropic) light of a suitable wavelength to crosslink the LCP material.

The configuration of this optical component is shown schematically in Figure 2.

It is also possible to use other types of hidden optical LPP/LCP devices, such as cholesteric LPP/LCP devices (of which an example is described later), "picture in picture" configured LPP/LCP devices such as described in International Application PCT/IB99/01810. Furthermore, the hidden optical device can be also positioned

between the evaporated aluminium layer and the thermochromic layer as shown in Figure 3 or between the thermochromic layer and the protective layer of the erasable and re-writable panel as shown in Figure 4.

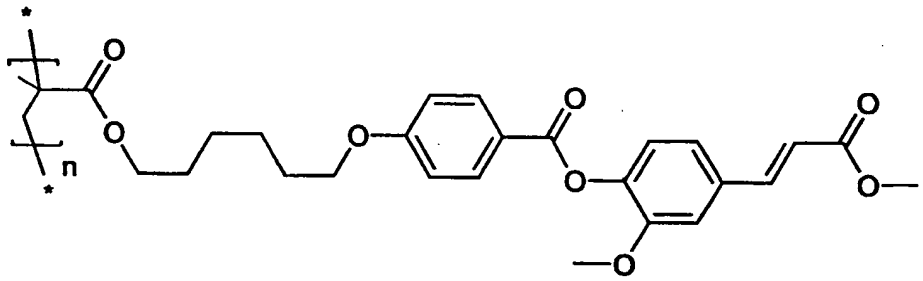
This completes the manufacture of these examples of the item according to the invention. When viewed normally (e.g. in particular without polariser) only the information stored into the thermochromic layer can be observed. The overlying normally hidden LPP/LCP image can be viewed by using a polariser.

The production of a linearly photopolymerised LPP and LCP layer which can be used according to the invention will be described, in more detail below, still by way of example.

Production of an LPP layer

Suitable LPP (PPN) materials are described for instance in patent publications EP-A-611786, WO 96/10049 and EP-A-763552, and include cinnamic acid derivatives and ferulic acid derivatives. For the foregoing Examples, the following LPP material was chosen:

Polymer:

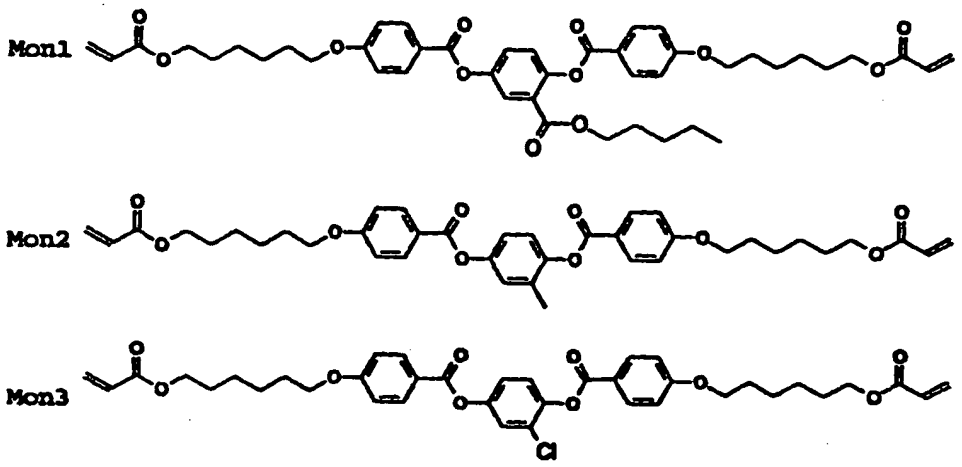


A glass plate was spin-coated with a 2 percent strength solution of the LPP material in MPK (methyl propyl ketone) for one minute at 2000 rpm. The layer was then dried for 5 to 10 minutes at 130 °C on a hotplate. The layer was then exposed to linearly polarised light from a mercury high-pressure lamp for 10 to 550 seconds (depending on the strength of the lamp and on the number of LPP/LCP layers of the

optical component) at room temperature. The layer was then used as an orientation layer for liquid crystals.

Mixture M_{LCP} of cross-linkable liquid crystal monomers for the LCP layer.

In the examples, the following diacrylate components were used as cross-linkable liquid crystal monomers:



Using these components, a supercoolable nematic mixture M_{LCP} with particularly low melting point (Tm ~ 35°C) was developed, making it possible to prepare the LCP layer at room temperature.

The diacrylate monomers were present with the following composition in the mixture:

Mon1 80%

Mon2 15%

Mon3 5%

In addition a further 2% of the Ciba-Geigy photoinitiator "Irgacure" (trade mark) was added to the mixture.

The mixture M_{LCP} was then dissolved in anisol. By varying means of the M_{LCP} concentration in the anisol, it was possible to adjust the LCP layer thickness over a

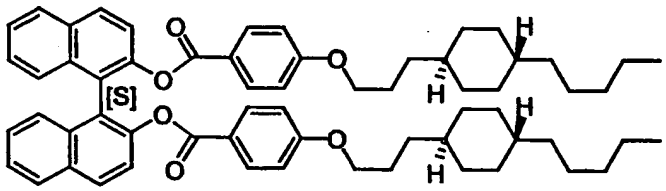
wide range. Especially for the examples of optical components described in this patent, the desired retardations Δnd of 0.13 to 0.14 μm could be achieved.

For photoinitiated cross-linking of the liquid crystal monomers, the layers were exposed to isotropic light from a xenon lamp for about 1 to 30 minutes (depending on the strength of the lamp) in an inert atmosphere.

Cholesteric LCP layer

For making a cholesteric LCP layer, a procedure similar to that of the nematic LCP layer was used. However, the mixture M_{LCP} was additionally doped with cholesteric material inducing a pitch. A suitable chiral dopant was e.g. ST31L, which shows a left-handed helical sense.

ST31L:



The concentration of the chiral dopant was for ST31L about 4% to 9%, more preferably 5 to 6%. This induces the desired reflective wavelength band in the visible range, but by changing the concentration also reflective wavelength bands in the UV or IR range can be realised. The substrate was coated with that cholesteric material by spin coating. The spin parameter are similar to those applied above. Of course also other printing or coating techniques can be applied, e.g. slot-coating, kbar-coating, etc.

The thickness of the cholesteric layer is 1 to 10 microns, depending on the wavelength range, more preferable from about 2 to 8 microns. Anisole is used as solvent. After the drying process on a hot plate (see above) the cholesteric LCP material containing a photo-initiator is cross-linked with isotropic UV light from a

xenon lamp for about 1 to 30 minutes (depending on the strength of the lamp) in an inert atmosphere.

The optical effects described above, as well as the corresponding layer structures and material compositions, represent only some of many possibilities according to the invention, and may in particular be combined in a wide variety of ways in order to develop authenticating elements.

Thus, it is of course possible for any other kind of birefringent layer than the LCP layer described to be used to produce an optical effect that can be employed in optical components, for example for authentication elements.

It is furthermore possible for the examples described above, to use not an LPP orientation layer but a different orientation layer which, according to the desired optical property and resolution, has the same or similar properties to an LPP layer. It is also conceivable to produce the orientation required for a retarder layer using a correspondingly structured substrate. A structured substrate of this type can, for example, be produced by embossing, etching and scratching.

A preferred embodiment of the invention will now be described, still by way of example. This embodiment uses a combination of (a) an item carrying rewritable information and (b) an LPP/LCP device *comprising a cholesteric layer*. This embodiment allows division of a visual object, such as a character or a picture, into two (patterned, non-discernible) parts, of which one is contained in the LPP/LCP device and the other can be written into the item carrying rewritable information. In this way, the visual object can only be discerned (observed through a polarizer) when the item carrying rewritable information has the pattern written in it that corresponds to the pattern contained in the LPP/LCP device.

Suitable rewritable materials for this embodiment are for instance the products BC650, 430AD (transparent PET) and BC650M, 430AC (white PET) from Ricoh Company Ltd.

BC650, 430AD is a clear and transparent film, which can be made opaque (black) when a particular temperature cycle is applied to the film (writing cycle).

Black images can be achieved by heating the film from ambient temperature to over 170°C ~ 190°C and cooling down to room temperature, the film areas are coloured by chemical reaction between a leuco dye and a developer in the recording layer (black state). By another temperature cycle the opaque (black) areas can be made again transparent (erasing cycle); an image or area of said film is erased by heating the film from room temperature to 120°C ~ 160°C and cooling down to room temperature, whereby the linkage between leuco dye and developer is broken and the film hence becomes discoloured (transparent).

BC650M, 430AC is a transparent film that is positioned on top of a white film. As with the BC650, 430AD film, the transparent film can be made opaque (black) when a particular temperature cycle is applied to the film (writing cycle) resulting in black images on a white background. By another temperature cycle the opaque (black) areas can be made again transparent (erasing cycle) resulting in a white appearance because of the white background.

For both films, the resolution can be quite high and depends on the printer head resolution, e.g. resolutions above 600dpi are achievable.

An LPP/LCP device, which advantageously can make use of the change in the absorption (from white to black) of such items carrying rewritable information, comprises a structured LCP layer on top of a cholesteric filter (e.g. a cholesteric LCP layer).

Figure 6 shows how the corresponding LPP/LCP device is arranged on top of the rewritable item, and an example of the optical mode of operation of this arrangement is schematically given in the subfigures, 6A, 6B and 6C. A particular new feature of such an arrangement is the possibility to visualise or recognise information stored in the cholesteric LPP/LCP device (schematically depicted in Fig. 6A) only when the correct information (pattern) is written into the leuco dye film (Fig. 6C).

The right graph in Fig. 6A shows schematically the phase pattern of the structured cholesteric LPP/LCP device. If all the segments or patterns of the back-stated leuco dye film are black then a pattern results like that one shown in Fig. 6B

when observed through a polarizer. By rotating the polarizer the pattern changes from positive to negative (6B left side and 6B right side, respectively). By doing so, only an optical effect is perceivable but no image or information can be recognised.

However, when the correct pattern (left graph of Fig. 6A) is written in the erasable and rewritable leuco dye film then an image or information is revealed in the combined devices; this is shown in Fig. 6C: in this example the characters 'OK' appear.

The embodiment comprising a cholesteric filter can be made as follows:

In a first step, a cholesteric LCP material is spin-coated (other coating or printing techniques are also applicable) onto a rewritable leuco dye film to form a layer, and subsequently exposed to UV light of suitable wavelength to be cross-linked.. The cholesteric LCP layer consists of a nematic liquid crystal layer which exhibits a helical twist configuration. The distance for a full 360 degrees turn determines the pitch p. Cholesteric filters exhibit selective reflection within a well-defined adjustable wavelength band and at the same time circularly polarise the light within the band. Within the selective reflection band, the circularly polarised component of incident light, which exhibits the same twisting sense (left-handed or right-handed) as the cholesteric helix is – in case that the thickness of the cholesteric layer is sufficiently thick, as a rule about 10 times the pitch p – totally reflected, whereas the opposite circularly polarisation is transmitted without attenuation. Outside of the selective reflection band the filter is fully transmissive and non-polarising. The cholesteric LCP layer of this preferred embodiment has a reflective wavelength band in the visible range, though for special applications the reflective wavelength band could also be in the IR or UV range. In case of the visible range, preferably the band is between 400 nm and 800 nm, more preferably between 450 nm and 650 nm. The cholesteric LCP material consists of a LCP mixture doped with dopant material which induces the necessary pitch for forming the desired reflective wavelength range.

Onto the cholesteric layer, an LPP layer, and then on the LPP layer an LCP layer, can be applied as already described herein.

Summary of features:

- Superposition of a normally hidden image (e.g. LPP/LCP security element of Rolic Ltd., Switzerland) and an erasable and re-writable panel (e.g. thermochromic cards from Ricoh Ltd., Tokyo, Japan) allowing simultaneously visualisation of both images (= "Optical Component"):
  - erasable and re-writable information or image is permanent visible
  - normally hidden image and/or information can be e.g. visualised with a polariser.
- The information or images in the erasable and re-writable panel of an item according to the invention can in principle be changed indefinitely, frequently without degrading the normally hidden image.
- The "Optical Component" according to the invention which is described above allows to make said cards much more secure.

CLAIMS

1. An item carrying rewritable visible information, characterised by a normally hidden image which can be revealed by means which do not tend to rewrite the visible information.

2. An item according to Claim 1, wherein the said means are light and a polariser.

3. An item according to Claim 1 or 2, wherein the normally hidden image is carried in at least one optically anisotropic layer having regions with different preferred directions.

4. An item according to any one of Claims 1 to 3, wherein the normally hidden image is carried in a liquid crystalline medium.

5. An item according to Claim 3, wherein the optically anisotropic layer is formed with cross-linked liquid crystalline monomers or pre-polymers.

6. An item according to Claim 4 or 5, which comprises an orientation layer for liquid crystal molecules.

7. An item according to Claim 6, wherein the orientation layer is formed of a linearly photopolymerised polymer network.

8. An item according to any preceding Claim, wherein the rewritable visible information is carried in a thermosensitive recording material.

9. An item according to Claim 8, wherein the thermosensitive recording material comprises a leuco dye and developer.

10. An item according to any preceding Claim, wherein the visible information co-operates with the normally hidden image to reveal other information.

11. An item according to any preceding Claim, which comprises a cholesteric filter.

12. An item according to any one of Claims 3 to 10, wherein a cholesteric filter is arranged between the optically anisotropic layer and the rewritable visible information.

FIGURE 1

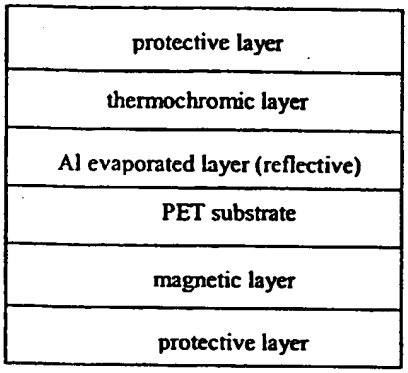


FIGURE 2

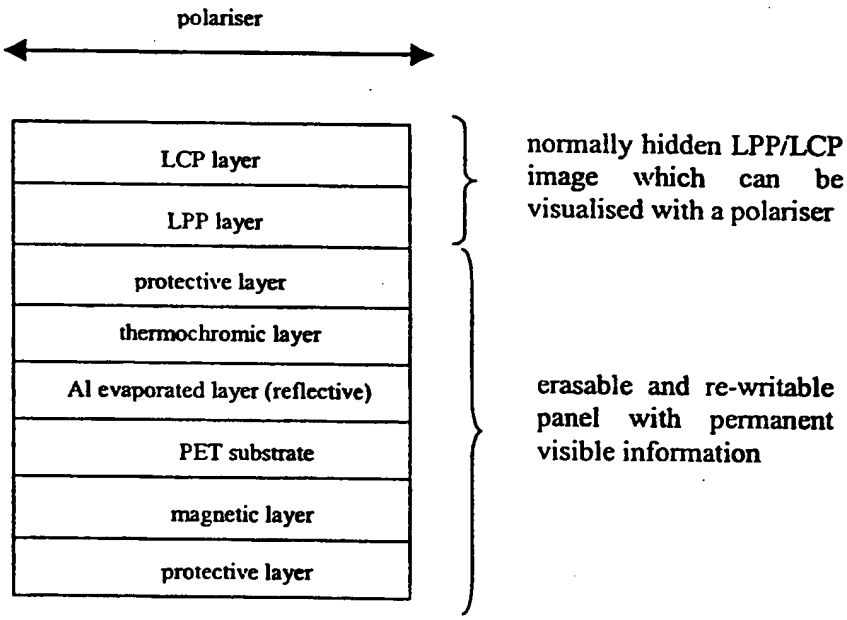


FIGURE 3

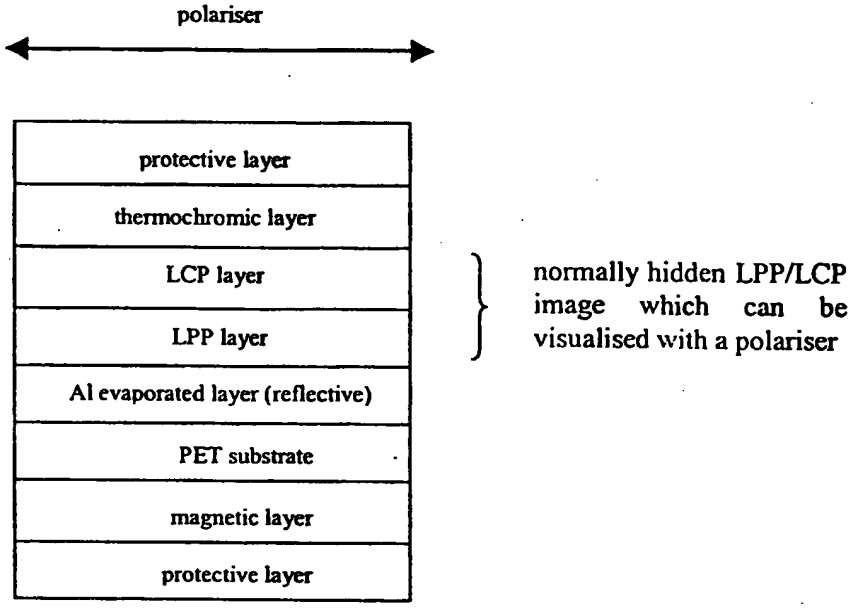


FIGURE 4

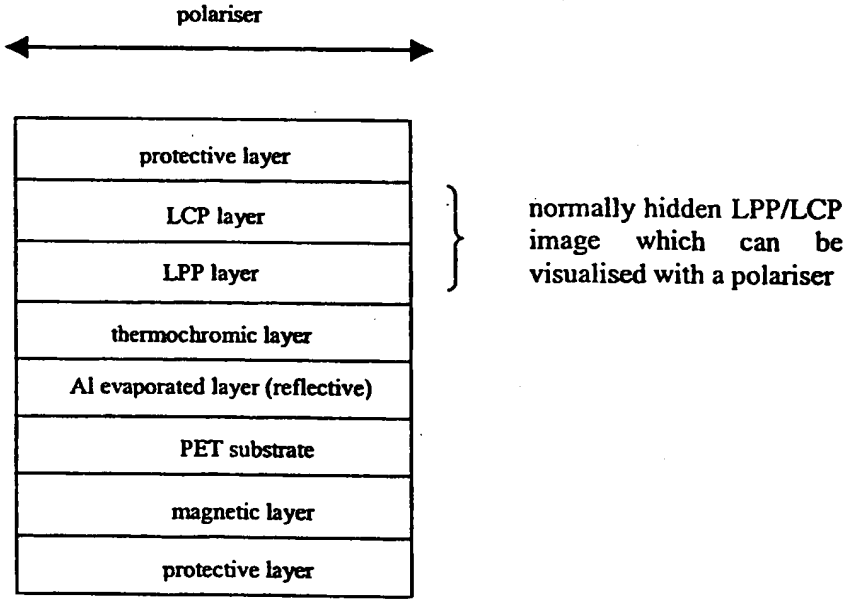


FIGURE 5

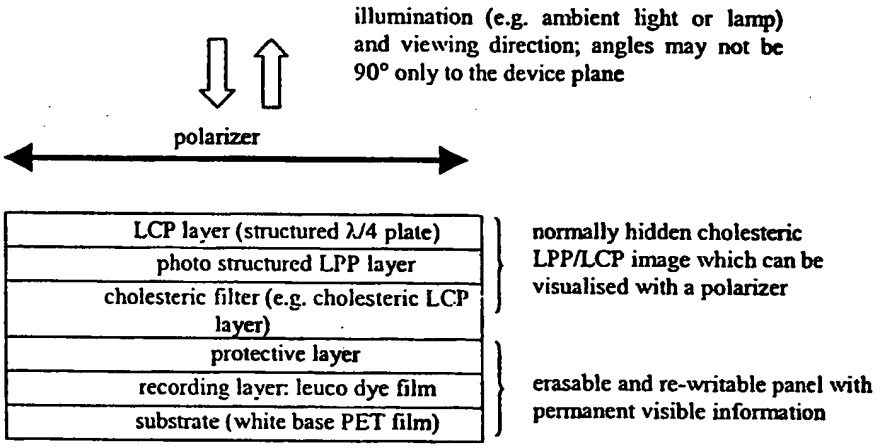
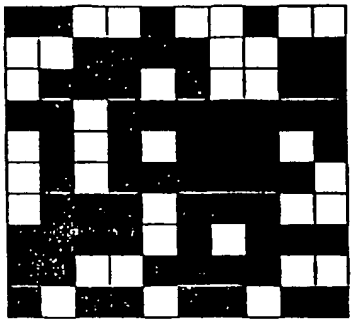

illumination (e.g. ambient light or lamp) and viewing direction; angles may not be 90° only to the device plane
polarizer
LCP layer (structured λ/4 plate)
photo structured LPP layer
cholesteric filter (e.g. cholesteric LCP layer)
protective layer
recording layer: leuco dye film
substrate (white base PET film)
normally hidden cholesteric LPP/LCP image which can be visualised with a polarizer
erasable and re-writable panel with permanent visible information

Fig. 6A

Leuco dye film (white base PET): printed pattern (no information can be recognised)



Cholesteric LPP/LCP Device (e.g.: CF filter: left handed) arrows depict the direction of the optical axis of the structured λ/4 LCP retarder

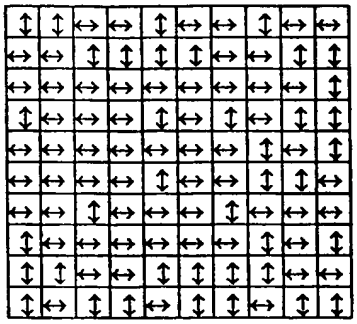


Fig. 6B

Optical appearance of above patterned cholesteric LPP/LCP device when the leuco dye film background is completely black, that means all 10 x 10 segments of the leuco dye layer are black [when the leuco dye film is erased (white state) then essentially no information can be seen].

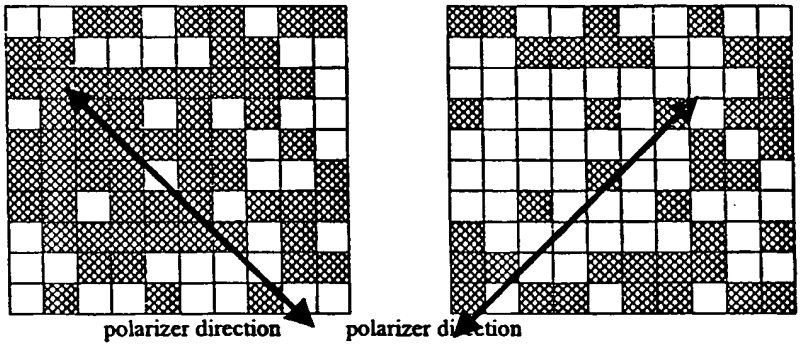
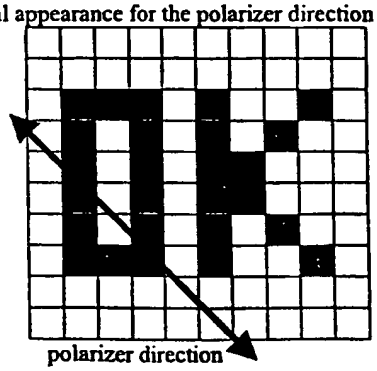


Fig. 6C

Combination of the Leuco dye (white base) and Cholesteric LPP/LCP device enables the recognition resp. the verification of the correct information of the cholesteric LPP/LCP security device (here the letters OK are shown): optical appearance for the polarizer direction –45°: positive image



INTERNATIONAL SEARCH REPORT

Interna[illegible]al Application No:
PCT/[illegible] 00/00329

A. CLASSIFICATION OF SUBJECT MATTER
G06K19/077

According to International Patent Classification (IPC) or to both national classification and IPC[7]

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G11B,G06K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0810590 A (IBM CORPORATION) 03 December 1997, page 5, line 27 - page line 14, fig. 1-5. --	1-10
A	EP 0651382 A (AKZO NOBEL N.V.) 03 May 1995, column 1, line 14 - column 5, line 53, fig. 2. --	1-9
A	US 5625446 A (BEDARD) 29 April 1997, claim 1, fig. 1-5. --	1
A	FR 2756954 A (SOLAIC SOCIETE ANONYME)	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 June 2000	25. 08. 2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	MIHATSEK

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IB 00/00329

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	12 June 1998, abstract, fig. 1-3. ----	

ANHANG	ANNEX	ANNEXE
Zum internationalen Rec...chenbericht über die internationale Patentanmeldung Nr.	To the International Search Report to the international Patent Application No.	Au rapport de recherche international relativ à la demande de brevet international n°
	PCT/IB 00/00329 SAE 273155	
In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.	This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.	La presénte annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsibilité de l' Office.

Im Recherchenbericht angeführte Patentdokumente Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A2 810590	03-12-1997	CN A 1167313	10-12-1997
EP A3 810590	09-06-1999	JP A2 10116441	06-05-1998
		US A 5761188	02-06-1998
EP A1 651382	03-05-1995	none	
US A 5625446	29-04-1997	none	
FR A1 2756954	12-06-1998	none	
FR B1 2756954	15-01-1999		